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On the lattice vibrations in cubic ionic crystals

By STIG O. LUNDQVIST

SUMMARY

This paper contains some further considerations connected with a previous paper in which the long polar oscillations of a cubic ionic lattice were discussed on the basis of a potential energy, which is a first approximation of the expression for the cohesive energy in the Heitler-London treatment of ionic crystals. A somewhat more accurate estimate of the three-body potential is considered here, giving certain correction terms to the formula for the effective charge derived earlier. The limitations of the Heitler-London method in this connexion are discussed and a semi-empirical approach is suggested including also the polarisation.

Introduction

Most earlier treatments of the vibrations of an ionic lattice have been based on the classical theory by Born, according to which the ions are regarded as rigid, non-polarizable structures interacting with central forces. It is now well known, however, that the assumptions inherent in the Born model are in general not fulfilled. For example, the Cauchy relations are in general not valid in ionic crystals even at zero temperature; furthermore it has become clear that the electronic polarisation plays an important role; and finally the study of the long polar oscillations has led to the introduction of an effective charge, which is known to be about 20 per cent smaller than the actual charge for the alkali halides. None of these features can be explained on the basis of the original Born model. This paper will present some considerations closely connected with a previous paper ([5], hereinafter referred to as A), and it will here be shown how the effects mentioned above can be taken into account in an approximate way.

In A a discussion of the vibrations was given, starting from a consideration of the expression for the binding energy in the Heitler-London approximation. In ionic crystals like NaCl and KCl the overlap between neighbouring ions is rather small so that the neglect of third and higher order terms in the overlap integrals is believed to be a fair approximation. Neglecting such terms an expression for the binding energy is obtained, which besides ordinary two-body interaction terms also contains terms representing the interaction between three ions. This is the approximation introduced by Landshoff [4] and which was later discussed in much detail by Löwdin [7], who first pointed out the occurrence of terms corresponding to many-body forces. Löwdin also calculated the elastic constants for several alkali halides taking such terms into account. The results show that the many-body forces provide a possible explanation of the deviation from the Cauchy relations in ionic crystals, although a discrepancy seems to exist between the observed and calculated value of the elastic constants. A different approach is due to Herpin [3], who investigated the polarizability forces and found that the quadrupole terms give rise to deviations from the Cauchy relations. The calculated deviations are, however, not in agreement with those found experimentally at low temperatures, even the sign is incorrect and thus it seems as these forces cannot alone be responsible for the deviations at low temperatures. The question about the deviations from the Cauchy relations seems not settled yet, but is intimately connected with the problem of finding a more accurate solution of the quantum mechanical many-body problem for a crystal. For the sake of simplicity we shall not consider the quadrupole forces investigated by Herpin but regard the deviations as due to the many-body terms occurring in the Heitler-London approximation.

In a discussion of the long polar oscillations of ionic crystals it was suggested by Lyddane, Sachs and Teller [6] that the actual ionic charge should be replaced by an effective charge. It was later pointed out by Szigeti [9] that the deviation from the actual charge might be due to the mutual distortion of neighbouring ions owing to their overlap. In another paper [10] he also derived a macroscopic relation from which the effective charge can be calculated from empirical data. In A it was shown that, using a very simple approximate expression for the three-body potential appearing in the Heitler-London approximation, an effective charge was introduced, which could be related to the elastic constants c_{12} and c_{44}. In this paper a more accurate estimate of the three-body potential will be used, giving rise to certain correction terms to the formula derived in *A*. The most obvious way to obtain the effective charge in this approximation, however, is to calculate the distortion moment from the formula for the charge density.[1]

It is well known that the electronic polarisation has to be included in order to obtain the correct limiting frequencies for the long polar oscillations and it seems certain that the polarisation will also influence the vibration modes of intermediate and short wavelengths. Unfortunately a satisfactory treatment of the polarisation does not exist, but one always assumes that the polarisation of the ions can be treated as if the field were homogeneous, having the same value as at the centre of the ion. Due to the strong inhomogeneity of the field around a lattice point it must be questioned whether such a treatment is at all permissible. For lack of a more satisfactory theory it will be used here as a device to obtain the correct limiting frequencies and one might at most hope that it might give the correct trend also for waves of intermediate and short wavelengths.

The potential energy

The discussion in this paper will be restricted to diatomic cubic ionic crystals of the NaCl type with ions having complete electron shells, and we shall assume (i) that only nearest neighbours overlap and (ii) that the overlap is so small that terms of third and higher orders in the overlap integrals can be neglected. For a more detailed discussion we refer to A and to the references given there. As in A we divide the potential energy of the lattice in the following three parts:

A. The classical electrostatic energy of the lattice, which is obtained by considering the ions as point charges

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[1] The writer is indebted to Prof. I. Waller for this remark.

$$\Phi_A = \frac{e^2}{2} \sum_G \sum_{G'}{}^{(G)} \frac{\varepsilon_G \varepsilon_{G'}}{|\mathbf{r}_G - \mathbf{r}_{G'}|}. \tag{1}$$

Here ε_G denotes the valency of the ion at the lattice point G and e is the elementary charge.

B. Terms depending only on the distance between two neighbouring nuclei

$$\Phi_B = e^2 \sum_G \sum_{G'} V'(|\mathbf{r}_G - \mathbf{r}_{G'}|). \tag{2}$$

C. Terms which correspond to a three-body potential. After some elementary transformations given in *A* these terms can be written

$$\Phi_C = 2e^2 \sum_\mu \sum_\nu \sum_G{}^{(G_\mu G_\nu)} \varepsilon_G S_{\mu\nu} (\nu G \mu)_{G_\mu} - \\ - e^2 \sum_\mu \sum_\nu \sum_G{}^{(G_\mu G_\nu)} \varepsilon_G S_{\mu\nu} S_{\nu\mu} (\mu G \mu). \tag{3}$$

Here μ denotes the orbital and spin quantum numbers of an electron associated with an ion at a lattice point G_μ. $S_{\mu\nu}$ are the overlap integrals

$$S_{\mu\nu} = \int \psi_\mu^*(x)\, \psi_\nu(x)\, d\tau - \delta_{\mu\nu}.$$

$\int d\tau$ implies integration over the space coordinates and summation over the spin coordinates and x means the space and spin coordinates of an electron ($x = \mathbf{r}, \zeta$). The symbol $(\nu G \mu)$ means the integral

$$(\nu G \mu) = \int \psi_\nu^*(x) \frac{1}{|\mathbf{r} - \mathbf{r}_G|} \psi_\mu(x)\, d\tau.$$

$(\nu G \mu)_{G_\mu}$ is obtained by splitting $(\nu G \mu)$ into two parts by dividing space in two nonoverlapping regions containing the lattice points G_μ and G_ν respectively so that

$$(\nu G \mu)_{G_\mu} + (\nu G \mu)_{G_\nu} = (\nu G \mu).$$

A simple approximate expression for the integrals $(\nu G \mu)_{G_\mu}$ and $(\mu G \mu)$ was obtained in A by assuming that the integrands are vanishingly small except in a small region around G_μ, so that the denominator $|\mathbf{r} - \mathbf{r}_G|$ can be approximated by $|\mathbf{r}_{G_\mu} - \mathbf{r}_G|$. A better approximation can be obtained by making use of the expansion of $|\mathbf{r} - \mathbf{r}_G|^{-1}$ in spherical harmonics around G_μ. The expansion contains both positive and negative powers of $|\mathbf{r}_{G_\mu} - \mathbf{r}_G|$, but terms with positive powers will be important only if the points G and G_μ are so close together that the integrand is appreciable outside a sphere with radius $|\mathbf{r}_{G_\mu} - \mathbf{r}_G|$). For crystals with small overlap the wave functions are well localized so these terms will be fairly small, and we shall for the sake of simplicity omit them in our discussion. Taking the first two terms in the expansion into account we obtain the following expression

$$\Phi_C = e^2 \sum_G \sum_{G'} \sum_{G''}{}^{(GG')} f_G(|\mathbf{r}_G - \mathbf{r}_{G'}|) \frac{\varepsilon_{G''}}{|\mathbf{r}_G - \mathbf{r}_{G''}|} + \\ + e^2 \sum_G \sum_{G'} \sum_{G''}{}^{(GG')} h_G(|\mathbf{r}_G - \mathbf{r}_{G'}|) \frac{\varepsilon_{G''} \cos \theta_{G''}}{|\mathbf{r}_G - \mathbf{r}_{G''}|^2}, \tag{4}$$

where

$$f_G(|\mathbf{r}_G-\mathbf{r}_{G'}|)=\sum_{\mu}^{G}\sum_{\nu}{}_{G'}\,(2\,\lambda_{\mu\nu}^{G}-1)\,S_{\mu\nu}\,S_{\nu\mu},$$

$$h_G(|\mathbf{r}_G-\mathbf{r}_{G'}|)=\sum_{\mu}^{G}\sum_{\nu}^{G'}2\,S_{\mu\nu}(\nu\,|\,r\cos\theta|)\,\mu_{G_\mu}),$$

$$S_{\nu\mu}\,\lambda_{\nu\mu}^{G_\mu}=\int_{G_\mu}\psi_\nu^*(x)\,\psi_\mu(x)\,d\tau.$$

Here θ denotes the angle between $\mathbf{r}$ and $\mathbf{r}_G-\mathbf{r}_{G'}$ and $\theta_{G''}$ is the angle between $\mathbf{r}_G-\mathbf{r}_{G'}$ and $\mathbf{r}_G-\mathbf{r}_{G''}$.

As in A it is convenient to include the two-particle terms corresponding to $G''=G'$ in the expression above and subtract the same terms from the two-body potential $V'(|\mathbf{r}_G-\mathbf{r}_{G'}|)$. Denoting the new two-body potential by $V(|\mathbf{r}_G-\mathbf{r}_{G'}|)$ we get the following formula for the potential energy:

$$\Phi=\frac{e^2}{2}\sum_{G}\sum_{G'}{}^{(G)}\frac{\varepsilon_G\,\varepsilon_{G'}}{|\mathbf{r}_G-\mathbf{r}_{G'}|}+e^2\sum_{G}\sum_{G'}V(|\mathbf{r}_G-\mathbf{r}_{G'}|)+$$

$$+e^2\sum_{G}\sum_{G'}\sum_{G''}{}^{(G)}f_G(|\mathbf{r}_G-\mathbf{r}_{G'}|)\frac{\varepsilon_{G''}}{|\mathbf{r}_G-\mathbf{r}_{G''}|}+$$

$$+e^2\sum_{G}\sum_{G'}\sum_{G''}{}^{(G)}h_G(|\mathbf{r}_G-\mathbf{r}_{G'}|)\frac{\varepsilon_{G''}\cos\theta_{G''}}{|\mathbf{r}_G-\mathbf{r}_{G''}|^2}. \tag{5}$$

The potential energy for small displacements

As the potential energy (5) is expressed in terms of the relative coordinates of the nuclei it seems most natural to expand it according to powers of the relative displacements of the nuclei. The treatment of the normal vibrations of a lattice, when a general potential is expanded in powers of the relative displacements of the nuclei, has been given by Waller [11] and we shall first review those of his formulae, which will be used in the following. In the expansion of Φ the second order term Φ_2 has the form

$$\Phi_2=\tfrac{1}{2}\sum_{ll'l''}\sum_{kk'k''}\sum_{\alpha\beta}\phi_{\substack{kk'k''\\ \alpha\beta}}^{l\,l'\,l''}\,u_{\substack{kk'\\ \alpha}}^{ll'}\,u_{\substack{kk''\\ \beta}}^{ll''}. \tag{6}$$

As usual the index l refers to a lattice cell, k denotes the particles in the cell and $u_{\substack{kk'\\ \alpha}}^{ll'}$ are the cartesian components of the relative displacements of the nuclei (l, k) and (l', k').

For crystals where each ion is a centre of symmetry, Waller has found the following expression for the elastic constants

$$C_{\alpha\gamma\beta\delta}=\frac{1}{\Delta}\sum_{l'l''}\sum_{kk'k''}\phi_{\substack{kk'k''\\ \alpha\beta}}^{l'l''}\,x_{\substack{kk'\\ \gamma}}^{l'}\,x_{\substack{kk''\\ \delta}}^{l''}, \tag{7}$$

where Δ denotes the volume of the elementary cell. It will be of use to have also the expansion in terms of the absolute displacements:

$$\Phi_2 = \tfrac{1}{2} \sum_{ll'} \sum_{kk'} \sum_{\alpha\beta} \overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}\, u^{l}_{\substack{k\\ \alpha}}\, u^{l'}_{\substack{k'\\ \beta}}, \tag{8}$$

the coefficients $\phi^{l\,l'\,l''}_{\substack{kk'k''\\ \alpha\beta}}$ and $\overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}$ being connected through the formula

$$\overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}} = - \sum_{l''k''} \{\phi^{ll''l'}_{\substack{kk''k'\\ \alpha\beta}} + \phi^{l'll''}_{\substack{k'kk''\\ \alpha\beta}} - \phi^{l''ll'}_{\substack{k''kk'\\ \alpha\beta}}\},\ l'k' \neq lk \tag{9}$$

$$\overline{\phi}^{ll}_{\substack{kk\\ \alpha\beta}} = - \sum_{l'k' \neq lk} \overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}.$$

The contributions from the first three sums in (5) have been discussed in detail in A, so we shall first discuss the last sum in (5), which we shall denote by Φ':

$$\Phi' = e^2 \sum_{G} \sum_{G'} \sum_{G''}^{(G)} \varepsilon_{G''}\, h_G(|\mathbf{r}_G - \mathbf{r}_{G'}|) \frac{\cos \theta_{G''}}{|\mathbf{r}_G - \mathbf{r}_{G''}|^2}. \tag{10}$$

Introducing a new quantity $g_G(r_{GG'})$ defined by

$$\frac{\partial g_G(r_{GG'})}{\partial x_{\substack{GG'\\ \alpha}}} = \frac{h_G(r_{GG'})}{r_{GG'}}\, x_{\substack{GG'\\ \alpha}},$$

$x_{\substack{GG'\\ \alpha}}$ being the components of $\mathbf{r}_{GG'}$, we can write (10) as

$$\Phi' = -e^2 \sum_{G} \sum_{G'} \sum_{G''}^{(G)} \sum_{\alpha} \varepsilon_{G''} \frac{\partial g_G(r_{GG'})}{\partial x_{\substack{GG'\\ \alpha}}} \frac{\partial}{\partial x_{\substack{GG''\\ \alpha}}} \left(\frac{1}{r_{GG''}}\right). \tag{11}$$

From (10) or (11) it follows that Φ' vanishes for an undisturbed lattice of the NaCl type.

The contribution to the coefficients $\phi^{ll'l''}_{\substack{kk'k''\\ \alpha\beta}}$ which we shall denote by $\phi'^{ll'l''}_{\substack{kk'k''\\ \alpha\beta}}$ can easily be found be expanding (11) and we find

$$\phi'^{l\,l'\,l''}_{\substack{kk'k''\\ \alpha\beta}} = -e^2 \{\varepsilon_{k''} [G^{ll'}_{kk'} T^{ll''}_{kk''}]_{\alpha\beta} + \varepsilon_{k'} [G^{ll''}_{kk''} T^{ll'}_{kk'}]_{\beta\alpha}\}, \tag{12}$$

where we have introduced the notations

$$G^{ll'}_{\substack{kk'\\ \alpha\beta}} = \left\{\frac{\partial^2 g_k(r^{ll'}_{kk'})}{\partial x^{ll'}_{\substack{kk'\\ \alpha}} \partial x^{ll'}_{\substack{kk'\\ \beta}}}\right\}_0 \quad \text{and} \quad T^{ll'}_{\substack{kk'\\ \alpha\beta}} = \left\{\frac{\partial^2}{\partial x^{ll'}_{\substack{kk'\\ \alpha}} \partial x^{ll'}_{\substack{kk'\\ \beta}}} \left(\frac{1}{r^{ll'}_{kk'}}\right)\right\}_0 \tag{13}$$

with

$$G^{ll}_{\substack{kk\\ \alpha\beta}} = 0 \quad \text{and} \quad T^{ll}_{\substack{kk\\ \alpha\beta}} = 0,$$

and where

$$[G^{ll'}_{kk'} T^{ll''}_{kk''}]_{\alpha\beta} = \sum_{\gamma} G^{ll'}_{\substack{kk'\\ \alpha\gamma}} T^{ll''}_{\substack{kk''\\ \gamma\beta}}.$$

The notation $\{\ \}_0$ indicates that the derivatives are evaluated at the equilibrium configuration.

Inserting the coefficients $\phi'^{\,ll'l''}_{\substack{kk'k''\\ \alpha\beta}}$ into the formula for the elastic constants (7) we find, noting that $\sum\limits_{l''k''} \varepsilon_{k''} T^{ll''}_{\substack{kk''\\ \gamma\beta}} x^{ll''}_{\substack{kk''\\ \delta}} = 0$, that Φ' gives no contributions to the elastic constants. This can also be seen directly from (10) or(11), because after an arbitrary homogeneous deformation each point is still a centre of symmetry and thus Φ' vanishes.

Adding the contributions from the first three sums in (5), which have been given in A, we obtain

$$\begin{aligned}\phi^{ll'l''}_{\substack{kk'k''\\ \alpha\beta}} = {} & e^2 \left[\tfrac{1}{2}\, \varepsilon_k \{\varepsilon_{k'} + 12\, f_{k'}(a_0)\}\, T^{ll'}_{\substack{kk'\\ \alpha\beta}} + V^{ll'}_{\substack{kk'\\ \alpha\beta}}\right] \delta_{l''l'}\, \delta_{k''k'} + \\ & + e^2 \left\{\frac{\partial f_k (r^{ll'}_{kk'})}{\partial x^{ll'}_{\substack{kk'\\ \alpha}}}\right\}_0 \left\{\frac{\partial}{\partial x^{ll''}_{\substack{kk''\\ \beta}}} \left(\frac{\varepsilon_{k''}}{r^{ll''}_{kk''}}\right)\right\}_0 + e^2 \left\{\frac{\partial f_k (r^{ll''}_{kk''})}{\partial x^{ll''}_{\substack{kk''\\ \beta}}}\right\}_0 \left\{\frac{\partial}{\partial x^{ll'}_{\substack{kk'\\ \alpha}}} \left(\frac{\varepsilon_{k'}}{r^{ll'}_{kk'}}\right)\right\}_0 - \\ & - e^2\, \varepsilon_{k''} [G^{ll'}_{kk'}\, T^{ll''}_{kk''}]_{\alpha\beta} - e^2\, \varepsilon_{k'} [G^{ll''}_{kk''}\, T^{ll'}_{kk'}]_{\beta\alpha},\end{aligned} \tag{14}$$

where we have introduced the notation

$$V^{ll'}_{\substack{kk'\\ \alpha\beta}} = \left\{\frac{\partial^2}{\partial x^{ll'}_{\substack{kk'\\ \alpha}}\, \partial x^{ll'}_{\substack{kk'\\ \beta}}} \left[V\, (r^{ll'}_{kk'}) + \frac{\alpha_M}{a_0}\, \varepsilon_k f_k (r^{ll'}_{kk'})\right]\right\}_0 . \tag{15}$$

Here α_M is the Madelung constant, and a_0 denotes the interionic distance in equilibrium.

By means of (9) we can now find the coefficients $\overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}$. Certain terms drop out because of the symmetry and we get

$$\overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}} = - e^2 \left[\varepsilon_k \{\varepsilon_{k'} + 12\, f_{k'}(a_0)\}\, T^{ll'}_{\substack{kk'\\ \alpha\beta}} + U^{ll'}_{\substack{kk'\\ \alpha\beta}} + 2 V^{ll'}_{\substack{kk'\\ \alpha\beta}} + W^{ll'}_{\substack{kk'\\ \alpha\beta}}\right], \tag{16}$$

where

$$U^{ll'}_{\substack{kk'\\ \alpha\beta}} = \sum_{l''k''} \left[\varepsilon_{k'} \left\{\frac{\partial f_{k''} (r^{ll''}_{kk''})}{\partial x^{ll''}_{\substack{kk''\\ \alpha}}}\right\}_0 \left\{\frac{\partial}{\partial x^{l''l'}_{\substack{k''k'\\ \beta}}} \left(\frac{1}{r^{l''l'}_{k''k'}}\right)\right\}_0 + \varepsilon_k \left\{\frac{\partial f_{k''} (r^{l'l''}_{k'k''})}{\partial x^{l'l''}_{\substack{k'k''\\ \beta}}}\right\}_0 \left\{\frac{\partial}{\partial x^{l''l'}_{\substack{k''k'\\ \alpha}}} \left(\frac{1}{r^{l''l}_{k''k}}\right)\right\}_0\right]$$

and

$$W^{ll'}_{\substack{kk'\\ \alpha\beta}} = \varepsilon_k [T\,G]^{ll'}_{\substack{kk'\\ \alpha\beta}} + \varepsilon_{k'} [T\,G]^{l'\,l}_{\substack{k'k\\ \beta\alpha}} - \sum_{l''k''} \{\varepsilon_{k'} [G^{ll''}_{kk''}\, T^{ll'}_{kk'}]_{\alpha\beta} + \varepsilon_k [G^{l'\,l''}_{k'k''}\, T^{l'\,l}_{k'k}]_{\beta\alpha}\},$$

where
$$[T\,G]^{ll'}_{\substack{kk'\\ \alpha\beta}} = \sum_{l''k''} \sum_{\gamma} T^{ll''}_{\substack{kk''\\ \alpha\gamma}}\, G^{l''l'}_{\substack{k''k'\\ \gamma\beta}}.$$

The effective charge

In A a formula for the effective charge was derived from the approximate expression for the three-body potential considered there. The inclusion of the additional term Φ' implies further contributions to the effective charge, which will be derived from (16). First, however, we shall derive the effective charge from the definition introduced by Szigeti [10] (cf. also Fröhlich [2]) by means of a certain dipole moment per unit volume for a small displacement **u** between the positive and negative ions

$$\mathbf{P} = N_0 e^* \mathbf{u},$$

N_0 being the number of cells per unit volume and e^* being the effective charge. According to the definition $\mathbf{P}$ is not the actual polarisation but the dipole moment obtained if the polarizing field acting on the ions is switched off, so that the total dipole moment is obtained by adding the contribution due to the electronic polarisation. In the Heitler-London approximation the electronic polarisation is neglected so we can calculate $\mathbf{P}$ from the charge density, which can be written

$$\mathbf{n}(\mathbf{r}) = \sum_G \left[Z_G e \,\delta(\mathbf{r} - \mathbf{r}_G) = \mathbf{n}_G(\mathbf{r})\right] + \underset{\text{overlap}}{\mathbf{n}(\mathbf{r})} \tag{17}$$

Here $Z_G e\,\delta(\mathbf{r} - \mathbf{r}_G) + n_G(\mathbf{r})$ is the charge density in a free ion with atomic number Z_G at the position $\mathbf{r}_G$, $\mathbf{n}_G(\mathbf{r}) = -e \sum_\zeta \sum_\mu^G |\psi_\mu(x)|^2$, $\sum_\zeta$ denotes the summation over the spin coordinate, and $\int n_G(\mathbf{r})\, d\mathbf{r} = -e N_G$, N_G being the number of electrons associated with the ion, $Z_G - N_G = \varepsilon_G$. The contribution from this part of the charge density to the polarisation is immediately found to be

$$\mathbf{P}_1 = N_0 \varepsilon e \mathbf{u}.$$

The overlap density is

$$\underset{\text{overlap}}{\mathbf{n}(\mathbf{r})} = e \sum_\zeta \sum_{\mu\nu} P_{\mu\nu} \psi_\nu^*(x)\, \psi_\mu(x), \tag{17'}$$

where

$$P_{\mu\nu} = S_{\mu\nu} - \sum_\varkappa S_{\mu\varkappa} S_{\varkappa\nu} \delta_{\mu\nu},$$

if we neglect quantities of third and higher orders in the overlap integrals.[1]

The contribution to the polarisation

$$\mathbf{P}_2 = \frac{e}{V} \sum_{\mu\nu} P_{\mu\nu} (\nu\,|\,\mathbf{r}\,|\,\mu),$$

V being the volume considered, can be simplified by writing $\mathbf{r} = \mathbf{r}_{G_\mu} + \boldsymbol{\rho}$ and noting that

$$\sum_\nu P_{\mu\nu} (1 + S)_{\nu\mu} = S_{\mu\mu} = 0$$

and that

$$(\mu\,|\,\boldsymbol{\rho}\,|\,\mu) = 0.$$

Thus

$$\mathbf{P}_2 = \frac{e}{V} \sum_{\mu\nu} S_{\mu\nu} (\nu\,|\,\boldsymbol{\rho}\,|\,\mu).$$

$S_{\mu\nu}(\nu\,|\,\boldsymbol{\rho}\,|\,\mu)$ is directed along the vector $\mathbf{r}_{G_\nu G_\mu}$, so writing

$$S_{\mu\nu} (\nu\,|\,\boldsymbol{\rho}\,|\,\mu) = m_{\mu\nu} \frac{\mathbf{r}_{G_\nu G_\mu}}{r_{G_\nu G_\mu}}$$

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[1] The product $\psi_\nu^*(x)\,\psi_\mu(x)$, $\mu \neq \nu$ is considered as a quantity of the order $S_{\nu\mu}$.

and summing over the μ and ν associated with G_μ and G_ν we find

$$\mathbf{P}_2 = \frac{e}{V} \sum_G \sum_{G'} m_G(r_{GG'}) \frac{\mathbf{r}_{G'G}}{r_{G'G}},$$

where
$$m_G(r_{GG'}) = \sum_\mu^G \sum_\nu^{G'} m_{\mu\nu}.$$

Considering small displacements $\mathbf{u}_G$ from the equilibrium positions of the nuclei and retaining only the terms linear in the displacements, we obtain

$$\mathbf{P}_2 = -\frac{e}{V} \sum_G \sum_{G'} \left\{ \frac{m_G(r_{GG'})}{r_{GG'}} \mathbf{u}_{GG'} + \left(m'_G(r_{GG'}) - \frac{m_G(r_{GG'})}{r_{GG'}} \right) \frac{\mathbf{u}_{GG'} \cdot \mathbf{r}_{GG'}}{r^2_{GG'}} \mathbf{r}_{GG'} \right\}.$$

The final summations can be easily performed, remembering that only nearest neighbouring overlap and that $\mathbf{u}_{GG'} = \mathbf{u}$ if G refers to a positive ion and $\mathbf{u}_{GG'} = -\mathbf{u}$ if G denotes a negative ion. Writing $m(a_0) = m_+(a_0) - m_-(a_0)$, where $m_\pm(a_0)$ are the moments associated with positive and negative ions respectively, we get

$$\mathbf{P}_2 = -N_0 e \left\{ \frac{4\, m(a_0)}{a_0} + 2\, m'(a_0) \right\} \mathbf{u}.$$

Introducing polar coordinates with the origin at the centre of the positive ion and the polar axes directed towards the negative ion we get

$$m(a_0) = \sum_\mu^{G_+} \sum_\nu^{G_-} \{ 2\, S_{\mu\nu} (\nu \,|\, r \cos\theta \,|\, \mu) - a_0 S_{\mu\nu} S_{\nu\mu} \}. \tag{18}$$

Adding $\mathbf{P}_1$ and $\mathbf{P}_2$ we find the effective charge

$$e^* = e \left[\varepsilon - 4 \frac{m(a_0)}{a_0} - 2\, m'(a_0) \right]$$

or writing $e^* = \varepsilon^* e$

$$\varepsilon^* = \varepsilon - \frac{4\, m(a_0)}{a_0} - 2\, m'(a_0). \tag{19}$$

A relation of this form has recently been derived by Born and Huang [1] from the assumption of a local distortion moment acting between neighbouring ions.

Another formula, which, although formally different, agrees with (19) up to second order in the overlap, can be derived from the coefficients $\overline{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}$ (16) in the following way. We consider two ions (l, k) and (l', k') at large distance from each other and neglect terms, which tend to zero as $(r^{ll'}_{kk'})^{-5}$ or faster. Then the first term in (16), representing a Coulomb interaction, will be retained, $V^{ll'}_{\substack{kk'\\ \alpha\beta}}$ represents the short range forces and gives no contribution. For large $r^{ll'}_{kk'}$ it was shown in A that

$$U^{ll'}_{\substack{kk'\\ \alpha\beta}} = 4\, \varepsilon_k\, a_0\, f'_{k'}(a_0)\, T^{ll'}_{\substack{kk'\\ \alpha\beta}}.$$

To obtain the expression for $W^{ll'}_{\substack{kk'\\ \alpha\beta}}$ for large $r^{ll'}_{kk'}$ we introduce the explicit expression for the quantities $G^{ll'}_{\substack{kk'\\ \alpha\beta}}$ and get

$$W^{ll'}_{\substack{kk'\\ \alpha\beta}} = \varepsilon_k \left\{ \frac{8\,(h_{\bar{k}'} - h_{k'})}{a_0} + 4\,(h'_{\bar{k}'} - h'_{k'}) \right\} T^{ll'}_{\substack{kk'\\ \alpha\beta}}.$$

Here $\bar{k}'$ refers to an ion of the opposite kind as k'.

For large $r^{ll'}_{kk'}$ we get for the coefficients $\bar{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}$

$$\bar{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}} = -e^2\,\varepsilon_k \left\{ \varepsilon_{k'} + 12\, f_{k'} + 4\,[a_0\, f'_{k'} + h'_{\bar{k}'} - h'_{k'}] + \frac{8}{a_0}\,(h_{\bar{k}'} - h_{k'}) \right\} T^{ll'}_{\substack{kk'\\ \alpha\beta}}$$

which represents a Coulomb interaction with the actual charge replaced by an effective charge $e^* = \varepsilon^* e$, where

$$\varepsilon^* = \left| \varepsilon_k \left[\varepsilon_{k'} + 12\, f_{k'} + 4\,(a_0\, f'_{k'} + h'_{\bar{k}'} - h'_{k'}) + \frac{8}{a_0}\,(h_{\bar{k}'} - h_{k'}) \right] \right|^{\frac{1}{2}}. \tag{20}$$

The unsymmetrical appearance of (20) results from the fact that we have neglected terms of third and higher orders in the overlap in the formula for the potential energy. By calculating the total electrostatic energy of the lattice from the formula for the charge density (17) and deriving the contribution to $\bar{\phi}^{ll'}_{\substack{kk'\\ \alpha\beta}}$, we should instead have obtained

$$\varepsilon^* = \left| \varepsilon_k + 6\, f_k + 2\,(a_0\, f'_k + h'_{\bar{k}} - h'_k) + \frac{4}{a_0}\,(h_{\bar{k}} - h_k) \right| \tag{21}$$

which agrees with (20) up to second order in the overlap integrals (note that the quantities f and h are of the second order in $S_{\mu\nu}$). Although (21) differs in form from (19), the two formulae can be shown to be identical by transforming the integrals in (21) to a coordinate system with the origin at centre of the positive ion and the polar axes directed towards the negative ion.

The formula given here can be compared numerically with that given by Szigeti [9], which is a macroscopic relation and thus independent of any specific model for the interaction between the ions. We have computed ε^* for NaCl according to (19) from the wave functions for free ions using tables for the radial integrals occurring, which were kindly placed at our disposal by Löwdin, and found the value $\varepsilon^* = 0.92$, which is the same value obtained by the approximate formula given in A. The value obtained by Szigeti, however, is considerably smaller, he found $\varepsilon^* = 0.74$ (at room temperature). This large discrepancy demonstrates clearly the poorness of the Heitler-London approximation. Although the lattice energies and interionic distances agree rather well with the empirical values, this is not the case with other properties, which depend more sensitively on the wave functions used. For that reason a calculation of the lattice vibrations cannot be successfully done of the basis on the energy terms calculated in the Heitler-London approximation. It seems therefore reasonable to try to determine the parameters appearing in such a way that the most important quantities like the interionic distance, the elastic constants and the effective charge will agree with experiment. It would of course be most desirable to consider interactions of a more general form than that used here, but unfortunately only a very limited number of parameters can be determined from empirical data. From the discussion in A and in this paper it follows that all parameters except the quantities h and its derivatives can be obtained from the elastic constants, the interionic distance and by using the equilibrium condition. The remaining parameters must be chosen so as to give the correct effective charge, but in addition one has to introduce some reasonable assumption as regards the overlap in order to assign definite values for these parameters.

Approximate treatment of the polarisation

It has been shown that the deviations from the Cauchy relations and the introduction of an effective charge are natural consequences of a quantum mechanical treatment according to the Heitler-London approximation, even though the numerical agreement is not very good. Nevertheless the treatment given here does not provide a satisfactory starting point for calculating the lattice vibrations, the main reason being that the Heitler-London approximation does not account for the electronic polarisation. From the study of the long polar vibrations it is well known that the neglect of the polarisation leads to incorrect limiting frequencies and it seems probable that also vibration modes of short and intermediate wavelength will be strongly influenced. Unfortunately a satisfactory treatment of the polarisation of ions in a lattice has not yet been given, but one always assumes that the polarisation can be calculated as if the field were homogeneous. Due to the finite extension of the ions and the strong inhomogeneity of the field this assumption seems far from justified, but nevertheless we shall make use of this assumption here and derive the contribution to the coefficients $\overline{\phi}^{ll'}_{\underset{\alpha\beta}{kk'}}$. A treatment for a general lattice has been given by Born and Huang [1], who consider waves and apply Ewalds transformation to the dipole field. Here we shall confine ourselves to a lattice of the NaCl type and by first considering a large but finite crystal instead of an infinite one the formal treatment can be made simpler.

The field at (l, k) due to a system of dipoles $\mathbf{p}^{l'}_{k'}$ associated with the other particles (l', k') is

$$E^{l}_{\underset{\alpha}{k}} = \sum_{l'k'} \sum_{\beta} T^{ll'}_{\underset{\alpha\beta}{kk'}}\, p^{l'}_{\underset{\beta}{k'}}. \tag{22}$$

We shall now calculate the exciting field, that is the field at the instantaneous position of (l, k) due to all the other particles. This field is the sum of three parts:

(i) The Coulomb field corresponding to the displacement of the nuclei l', k'), which is obtained by putting $\mathbf{p}^{l'}_{k'} = e^{*}_{k'}\,\mathbf{u}^{l'}_{k'}$

(ii) The field due to the induced dipoles: $\mathbf{p}^{l'}_{k'} = \boldsymbol{\mu}^{l'}_{k'}$

(iii) The field change owing to the displacement of the particle (l, k) itself, which can be calculated as if the particle is kept fixed and that all other particles are subjected to a displacement $-\mathbf{u}^{l}_{k}$, thus $\mathbf{p}^{l'}_{k'} = -e^{*}_{k'}\,\mathbf{u}^{l}_{k}$.

Denoting the exciting field by $\mathbf{E}^{l}_{k}$ we then obtain

$$E^{l}_{\underset{\alpha}{k}} = \sum_{l'k'} \sum_{\beta} T^{ll'}_{\underset{\alpha\beta}{kk'}} \left(e^{*}_{k'}\, u^{l'l}_{\underset{\beta}{k'k}} + \mu^{l'}_{\underset{\beta}{k'}}\right). \tag{23}$$

We introduce the notation

$$E^{0}{}^{l}_{\substack{k\\ \alpha}} = \sum_{l'k'} \sum_{\beta} T^{ll'}_{\substack{kk'\\ \alpha\beta}}\, e^{*}_{k'}\, u^{l'l}_{\substack{k'k\\ \beta}}$$

for the Coulomb contribution and put

$$\boldsymbol{\mu}^{l'}_{k'} = \alpha_{k'}\, \mathbf{E}^{l'}_{k'},$$

$\alpha_{k'}$ being the polarizability for particles of type k' and $\mathbf{E}^{l'}_{k'}$ being the exciting field at (l', k'). Then we get instead of (23)

$$E^{l}_{\substack{k\\ \alpha}} = E^{0}{}^{l}_{\substack{k\\ \alpha}} + \sum_{l'k'} \sum_{\beta} T^{ll'}_{\substack{kk'\\ \alpha\beta}}\, \alpha_{k'}\, E^{l'}_{\substack{k'\\ \beta}}. \tag{24}$$

To solve (24) it is convenient to regard the quantities in it as elements of matrices and column vectors in $3N$-dimensional space, N being the number of ions in the crystal. Thus introducing the matrices $\mathbf{T}$ and $\boldsymbol{\alpha}$, where

$$\alpha^{ll'}_{\substack{kk'\\ \alpha\beta}} = \alpha_{k'}\, \delta_{ll'}\, \delta_{kk'}\, \delta_{\alpha\beta}$$

and the vectors $\mathbf{E}$ and $\mathbf{E}^0$, we get

$$\mathbf{E} = \mathbf{E}^0 + \mathbf{T}\,\boldsymbol{\alpha}\,\mathbf{E}. \tag{25}$$

If $\det(1 - \mathbf{T}\alpha) \neq 0$, which we shall assume, we get the formal solution

$$\mathbf{E} = (\mathbf{1} - \mathbf{T}\,\boldsymbol{\alpha})^{-1}\,\mathbf{E}^0. \tag{26}$$

Now the force on the particle (l, k) due to the field is simply $e^{*}_{k}\mathbf{E}^{l}_{k}$. This includes the classical coulomb field as well as the coulomb part of the many-body interactions, which we have already considered. The additional force due to the polarisation is found by subtracting the field $\mathbf{E}^0$, thus

$$K^{l}_{\substack{k\\ \alpha}} = e^{*}_{k}\{\mathbf{T}\,\mathbf{Q}\,\mathbf{E}^0\}^{l}_{\substack{k\\ \alpha}}, \tag{27}$$

where we have introduced the symbol

$$\mathbf{Q} = \left\{\frac{\mathbf{1}}{\boldsymbol{\alpha}} - \mathbf{T}\right\}^{-1}. \tag{27'}$$

Inserting the expression for the coulomb field $\mathbf{E}^0$ we can easily find from (27) the coefficients $\overline{\phi}^{Pll'}_{\substack{kk'\\ \alpha\beta}}$ associated with the polarisation forces

$$\overline{\phi}^{Pll'}_{\substack{kk'\\ \alpha\beta}} = -e^{*}_{k}\, e^{*}_{k'}\, \{\mathbf{T}\,\mathbf{Q}\,\mathbf{T}\}^{ll'}_{\substack{kk'\\ \alpha\beta}}. \tag{28}$$

Neglecting surface effects these quantities will not depend on l and l', but only on the difference l–l'.

The polarisation forces can alternatively be derived from the following expression for the potential energy

$$\Phi^{P} = -\tfrac{1}{2}\,\mathbf{E}^0\,\mathbf{Q}\,\mathbf{E}^0. \tag{29}$$

which can easily be reduced to the standard form (6), giving the coefficients

$$\phi^{Pll'l''}_{\substack{kk'k'' \\ \alpha\beta}} = -e^*_{k'}\, e^*_{k''} \{T^{ll'}_{kk'}\, [Q\, T]^{ll''}_{kk''}\}_{\alpha\beta}. \tag{30}$$

The coefficients $\bar{\phi}^{Pll'}_{\substack{kk' \\ \alpha\beta}}$ can be calculated according to (9) and noting that sums of the type $\sum\limits_{l'k'} e^*_{k'}\, T^{ll'}_{\substack{kk' \\ \alpha\beta}}$ vanish, we immediately get (28).

Inserting (30) in the formula for the elastic constants (7) we find that the polarisation forces do not contribute to the elastic constants.

The discussion given here has been based on the formal solution (26), but the coefficients $\bar{\phi}^{ll'}_{\substack{kk' \\ \alpha\beta}}$ can hardly be computed according to (28) because of the difficulties in performing the matrix inversions and multiplications. In order to investigate the lattice vibrations, however, we only need the associated Fourier matrix. This is fortunately rather easy to calculate, for by making use of the faltung property the calculation will be reduced to operations on 6 × 6 matrices, which can be handled by standard methods.

In A the polarisation was included for the long optical vibrations by means of certain macroscopic relations involving the dielectric constants for static and high-frequency fields, and formulae for the transverse and longitudinal frequencies were derived, which were generalisations of those given independently by Odelevski [8] and Szigeti [10] for the case of central forces. These formulae can now be obtained from (16) and (28) by neglecting the non-coulomb part of the many-body terms in (16) and by making use of the relations between the elastic and dielectric constants and the parameters in (16) and (28). A corresponding derivation has been given by Born and Huang [1] in the case of central forces, so the details will not be given here.

Comments

In this paper a set of formulae have been derived from which the lattice vibrations of ionic lattices of the NaCl type can be calculated, allowing for the effects of the deviations from the Cauchy relations, the effective charge and the electronic polarisation. An accurate treatment of this problem would require an accurate solution of the quantum mechanical many-body problem for a crystal and therefore a semi-empirical approach has been suggested here, based mainly upon the Heitler-London approximation. The Heitler-London approximation leads without extra assumptions to deviations from the Cauchy relations of the correct sign and order of magnitude and to the introduction of an effective charge, although the form of the potential considered here is certainly too restrictive. From several points of view, however, the approach suggested here is not very satisfactory. The terms in the potential energy, which are associated with the deviations from the Cauchy relations and the effective charge, are derived from a very approximate quantum mechanical treatment and the polarisation has been treated on a classical model. It seems not at all obvious that the potential energy derived from an accurate quantum mechanical treatment of the crystal could to a fair degree of approximation be reduced to the simple form discussed here. Therefore, the treatment given here ought to be considered more as a phenomenological theory, the aim of which is only to take into account certain features not considered in the classical Born model.

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Institute for Theoretical Physics, University of Uppsala.

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